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Redox polymer as an adsorbent for the removal of chromium (VI) and lead (II) from the tannery effluents

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ABSTRACT

Polymer-based hybrid was widely fabricated and applied in heavy metal removal and other inorganic pollutants. The present study deals with the sorption efficiency of metal adsorption through the chemically modified PAA with dihydroxybenzenes into the polymeric matrix present in the tannery effluents and a parallel investigation of chromium (VI) ions in aqueous solution was carried out. From the Langmuir model the removal of chromium (VI) has the maximum adsorption capacity with 181.4 mg g^{-1}. Batch sorption to remove chromium (VI) and lead (II) from the tannery effluents was investigated by using different parameters. The sorption efficiency was found to be 75% and 99% for chromium (VI) and lead (II), respectively, present in the tannery effluents. The chemical and structural characteristics of the adsorbents were determined by UV, FT-IR, TGA, DSC, XRD and SEM-EDS analyses.

1. Introduction

The pollutant from the tannery industries produces wide varieties of high strength toxic chemicals. During the chrome tanning process, 40% unused chromium salts are usually discharged in the final effluents, causing a serious threat to the environment [1]. Metal ions in the environment bioaccumulate and are biomagnified along the food chain. One of the important features that distinguish heavy metals from other pollutants is that the former are non-biodegradable. Once metal

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ions enter the environment, their chemical form largely determines their potential toxicity [2,3]. In aqueous phase chromium exits in two oxidation states such as trivalent chromium (i.e., Cr^{3+}, or $Cr(OH)^{2+}$) and hexavalent chromium (i.e., $HCrO_4^-$, CrO_4^{2-} or $Cr_2O_7^{2-}$). Chromium (VI) is very toxic to living organisms than Cr(III) [4–6]. Chromium (III) is essential for human nutrition (especially in glucose) and it is relatively innocuous and immobile. Chromium (VI) ions cause epigastric pain, nausea, vomiting, severe diarrhea, hemorrhaging and are nephrotoxic, mutagenic and carcinogenic. Chromium (VI) ions are notoriously mobile in nature because they are weakly bound to the inorganic surface [7,8]. Lead (II) is one of the most toxic heavy metals causing health problems such as behavioral anomaly, learning disabilities and seizures. Low level of lead (II) has been identified with anemia while high level causes severe dysfunction of kidneys, liver, central and peripheral nervous system, the reproductive system and high blood pressure [9]. Therefore the World Health Organization (WHO) recommends the toxic limits of chromium (VI) and lead (II) in waste water to the level of 0.05 mg L^{-1} [10] and 0.0015 mg L^{-1} respectively [11].

Polymers with redox units, being either integral parts of the polymer matrices or attached ones are distinguished by oxydo-reduction chemistry features. Of the redox entities are organometallics such as metallocenes and organics such as pyridinium salts and hydroquinone or catechol [12]. They are usually attached with functional groups of the redox-type either as pendant groups from polymer matrix or being part of the polymer chain. The redox polymers exhibit redox properties, metallic adsorption through their chelating ability [13,14]. Polymeric adsorbents are superior to other solid adsorbents due to their vast surface area, adjustable surface chemistry, and feasible regeneration under mild conditions. Polymers with specific functionalities can be obtained, by either synthesizing new monomers bearing the functional groups capable of interacting with the target metal ions, followed by polymerization, or by converting the groups on the existing polymers or co-polymers with suitable chemical reactions into the desired functional groups. Imidazo and amidoxime functional groups have been incorporated in the polymer backbone to adsorb various metal ions from aqueous solutions [15]. By incorporation of appropriate functional groups into the ion-exchanger matrix, its selectivity for chromium and lead can be enhanced. The catechol groups can form strong hydrogen bonds with other materials and therefore, catechol is widely used to design functional polymers [16]. In the present study, an attempt was made to synthesize redox polymer with polyacrylic acid and was integrated with catechol–hydroquinone. The synthesized redox polymers were used for the adsorption of heavy metals like chromium (VI) and lead (II) from the tannery effluents and the adsorption capacities were compared with the chromium ions in aqueous solution.

2. Materials

All the chemicals were purchased from Merck and Aldrich and were used as received.

2.1. Characterization

The viscometric measurements were performed in dioxane at 30 °C using Cannon Ubbelohde capillary viscometer. The average molecular weights (Mv) were estimated by the standard relation of Mark–Houwink–Sakurada [17]. UV–Vis spectra were recorded using a UV–Vis spectrophotometer, Systronics. Infrared spectra were taken with a Bruker FT-IR. X-ray diffraction measurement was carried out using Diffractometer system XPERT-PRO with Cu Kα radiation ($\lambda = 0.154$ nm) at the scanning rate of 2°/min. The thermal studies were recorded on SDT Q600 V8.3 build 101 with the heating rate of 10 °C min^{-1} under nitrogen atmosphere. The scanning electron micrographs and EDS of polymer samples have been scanned at 5000 × to 10,000 × magnification at the accelerating voltage of 10 kV with the working distance of 10 mm by FEI Quanta FEG 200 High Resolution SEM-EDS. The concentration of the chromium and lead metal ions of the tannery effluents was estimated through Perkin Elmer Optima 5300 DV ICP-OES at the wavelength of 267.716 nm and 220.353 nm respectively.

The study area was comprised in Vellore district situated on the North east part of Tamil Nadu. Effluent (1) and Effluent (2) were collected in the tanneries located at 12.78°N–78.7°E, and 12.68°N–78.62°E respectively.

2.2. Synthesis and chemical modification of polyacrylic acid

Polyacrylic acid (PAA) was synthesized via a radical polymerization using hydrogen peroxide as radical initiator and potassium dichromate was used as an oxidant for the synthesis of chemically modified PAA. The standard procedure [18] with slight modification was adopted in the synthesis and chemical modification of PAA and the percentage of substitution were calculated from the absorbance value. The scheme had been illustrated in Fig. 1.

The percentage of substitution was calculated by the formula

$$S(\%) = \frac{n_{VHQ}}{n_{AA} + n_{VHQ}} \times 100 \tag{1}$$

$$n_{AA} = \frac{m - n_{HQ} M_{VHQ}}{M_{AA}} \tag{2}$$

where n_{VHQ} = number of moles of hydroquinone and catechol (in the form of vinylhydroquinone and vinylcatechol) present in PAA-HQ, estimated from the UV calibration curve
n_{AA} = number of moles of acrylic acid present in PAA-HQ, provided by Eq. (2)
m = sample weight of PAA-HQ used in the UV measurement
M_{AA} and M_{VHQ} are the molecular weights of acrylic acid and vinylhydroquinone (or vinylcatechol).

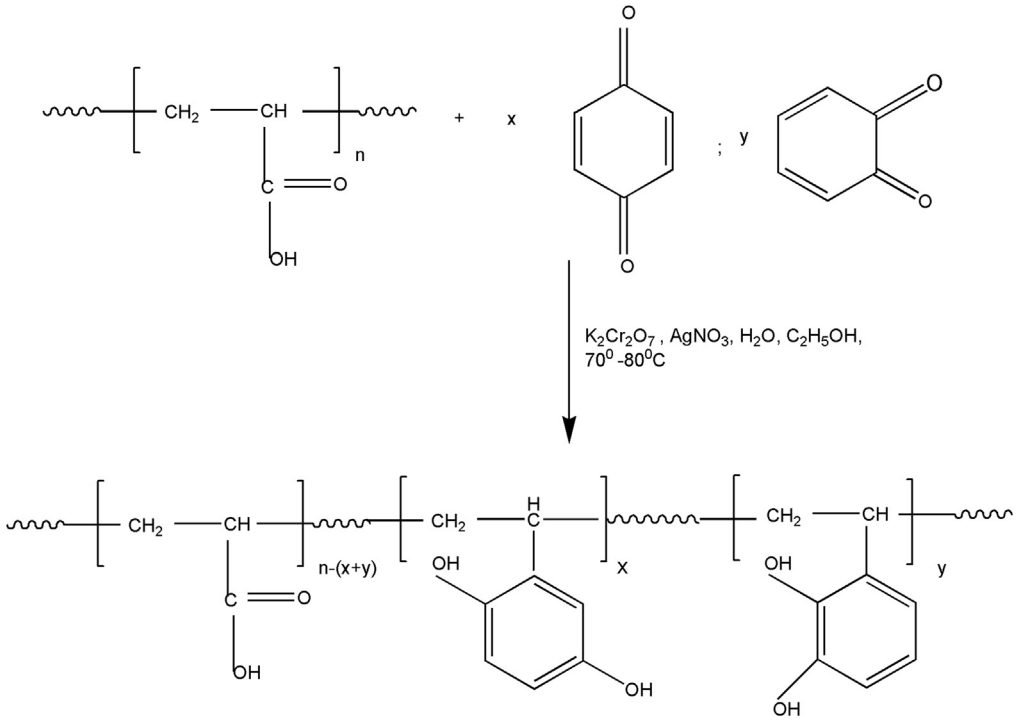

Fig. 1. Reaction scheme of the chemical of PAA by Catechol–Hydroquinone.

2.3. Batch adsorption experiment

Adsorption experiment was carried out in batch mode at the temperature of 25 °C in order to investigate the interaction between Cr (VI) and the chemically modified PAA. The effect of pH on removal of chromium was carried out, followed by further search for the influence of the effect of initial concentration and adsorption dosage on adsorption capability at the optimized pH value. Rotary shaker was used at the speed of 200 rpm. After completion of every set of experiments the concentration of Cr (VI) in solution was measured spectrophotometrically at λ 540 nm using diphenylcarbazide which forms a red–violet colored complex [19].

The data obtained in the batch studies were used to calculate the metal adsorptive capacity by using the following mass balance relationship:

$$q_e = ((C_0 - C_e)V)/m \tag{3}$$

The metal ion removal percentage can be calculated as follows:

$$\%\,\text{Removal} = ((C_0 - C_e)/C_0) \times 100 \tag{4}$$

C_0 and C_e are the initial and equilibrium concentrations (mg L^{-1}) of the metal ions respectively. V (mL) is the volume of the metal ion solution, and m is the mass of adsorbent (mg).

2.4. Adsorption isotherm studies

Isotherm models like Langmuir, Freundlich, Dubin and Radushkevich and Temkin models were tested for equilibrium description [20].

3. Results and discussion

3.1. Percentage of substitution and molecular weight determination

The percentage of the aromatic moieties incorporated into the polymeric chain of PAA was found to be 91% for PAA/Catechol–Hydroquinone at the end of 7 h (Fig. 2). The average molecular weight of PAA and PAA/Catechol–Hydroquinone was found to be 5.8×10^5 g mol^{-1} and 1.01×10^7 g mol^{-1} with the η value of 0.58 and 0.76 dL g^{-1} respectively. It is observed that, as the percentage of substitution increased, the average molecular weight increased linearly from pure PAA to chemically modified PAA. The higher percentage of substitution is due to the PAA longer chains linked with the dihydroxybenzene moieties [21].

3.2. Characterization of chemically modified PAA

3.2.1. TGA of chemically modified PAA

Pure PAA in Fig. 3(a) shows a three-stage degradation process. A first weight loss of about 6% occurs within the range 100–150 °C and is related to the formation of intra- and inter-molecular anhydride bonds with a consequent loss of water. A second weight loss of about 26% occurs in the range 200–300 °C and is related to the decarboxylation process of the anhydride bonds formed in the previous stage. A third weight loss occurs within the range 650–750 °C and is related to the full degradation of the macromolecule [22]. Chemically modified PAA was found to proceed in three step weight losses (Fig. 3(a)). The least stable step (around 110 °C) would be initiated by scissions of head-to-head linkages (H–H). The second step with the apparent weight loss was described as initiated by scissions at unsaturated ends with 25% of weight loss. At higher molecular weights, first-order termination could occur. For the present work, the side chain elimination was an initiation route for depropagation

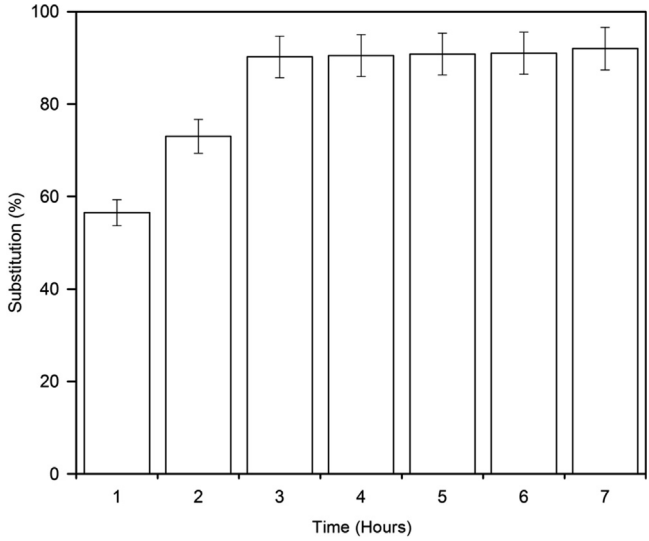

Fig. 2. Effect of time on the percentage of substitution to synthesize chemically modified PAA under the following conditions: temperature 80 °C and reaction time of 7 h.

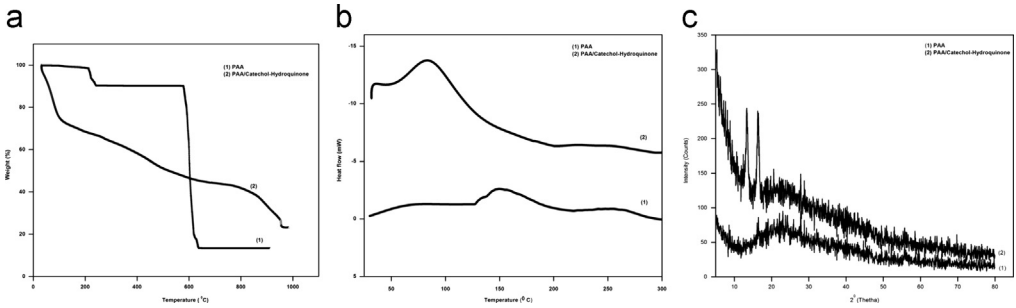

Fig. 3. Characterization of PAA and chemically modified PAA. (a) TGA, (b) DSC and (c) XRD.

because the amount of char produced during this work exceeds 15% leading to the weight loss of dihydroxybenzene moieties. The last step of decomposition at 750 °C was initiated by random scission within the polymeric chain [23]. The thermal studies account that, up to 110 °C, the chemically modified PAA can be capable of being an adsorbent. After 110 °C, the side chain elimination of the dihydroxybenzene moieties take place.

3.2.2. DSC of PAA and chemically modified PAA

The DSC of PAA has the Tg at 143 °C and for PAA/Catechol–Hydroquinone it was 87.14 °C shown in Fig. 3(b). The introduction of the dihydroxybenzene moieties into the backbone of PAA leads to a decrease in polymer chain rigidity as shown by the decrease in Tg of the chemically modified PAA and there exists a strong interaction between the polymeric backbone and the aromatic moieties [24,25]. One interesting observation is that the maximum graft (percentage of substitution) yield occurs for a temperature near the glass transition temperature [26]. The Tg around 80 °C from the DSC studies reveals that the maximum percentage of substitution occurred when the reaction was maintained at 80 °C for the oxidant $K_2Cr_2O_7$ when compared to chemically modified PAA synthesized from potassium persulphate as an oxidant [18].

3.2.3. XRD studies

The XRD patterns of the PAA and chemically modified PAA are given in Fig. 3(c). PAA exhibits amorphous behavior due to the large size of the PAA chains which makes it difficult for the orderly packing of chemically modified PAA chains and thus the crystalline nature of the chemically modified PAA is impossible [27]. From Fig. 3(c) two similar peaks at 0.492° and 0.5904°and d-spacing of 6.627 Å and 5.4118 Å with a grain size of 3.940 nm and 3.284 nm were observed. There was a distinct crystalline peak around 20° in XRD patterns of the PAA/Catechol–Hydroquinone. It is probably because plenty of –OH groups exist in the catechol and hydroquinone structures, which can form strong intermolecular and intra-molecular hydrogen bonds, and thus the PAA/Catechol–Hydroquinone forms crystalline regions easily. However compared to chemically modified PAA, the chemically modified PAA loaded Cr (VI) and Pb (II) when introduced into the polymeric main chains would destruct the intermolecular and intra-molecular hydrogen bonds and certain regularity of the modified polymer [28].

3.3. Adsorption of heavy metals

3.3.1. Influence of pH

The pH is one of the important parameters in the adsorption of heavy metals and at lower pH, the OH of the chemically modified PAA is be fully protonated; thus the adsorbent is inactive for the uptake of other heavy metals ions [29] and in acidic media, $HCro_4^-$, Cro_4^{2-} and H_2Cro_4 are the predominant species. In basic solutions chromium exists in the form of CrO_4^{2-}. If the pH ranges from 2 to 6, $HCro_4^-$ and $Cr_2O_7^{2-}$ are predominant in equilibrium; but at pH < 1 the main species are H_2CrO_4 [30].

At acidic pH of 1, the adsorption efficiencies were found to be 93% (Fig. 4(a)). There is a sharp decrease in percentage adsorption with increase in pH. At lower pH, the surface of the adsorbent is more protonated and this results in the stronger attraction of the negatively charged Cr(VI) complex ions into the solution. Adsorption of chromium at pH 1.0 shows the binding of negatively charged chromium species $HCro_4^-$ through the electrostatic attraction to the positively charged (due to the more H^+) surface. As the pH increases, the protonated surface leads to the weakening of adsorption. For pH > 6.0, CrO_4^{2-} is the predominant form because of the high repulsion by high negative surface [31] and at pH of 4 and 6 the predominant chromium species are $HCro_4^-$ and CrO_4^{2-} and the hydroxyl groups of the chemically modified PAA do not ionize and hence the uptake of chromium on this polymer is due to the complex formation on to the polymer matrix [32].

3.3.2. Influence of contact time on adsorption

The adsorption of Cr (VI) increased as the contact time increased for the modified PAA and the maximum adsorption was found to be 85% at the end of 10th hour with the adsorbent dosage of 100 mg L^{-1}. The increase in adsorption efficiency at higher time for the modified PAA with dihydroxybenzenes may be attributed to the higher percentage of substitution [33]. The increase in the percentage of substitution leads to higher surface area and more active sites when compared to

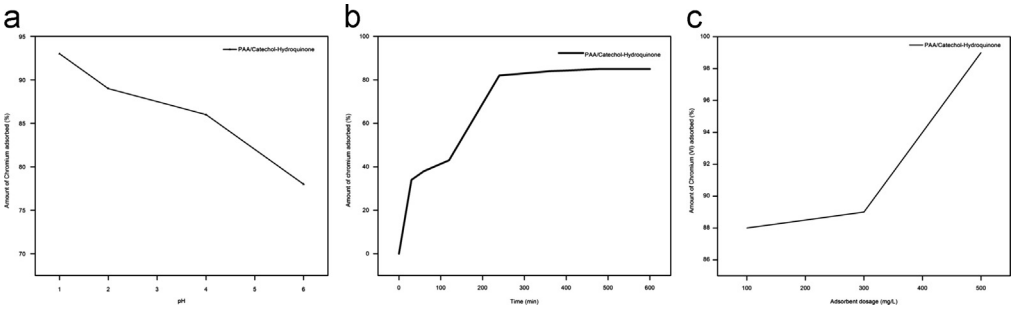

Fig. 4. Adsorption of chromium on to the chemically modified PAA. (a) Effect of pH, (b) effect of contact time and (c) influence of the adsorbent dosage.

Table 1
Isotherm parameters for the adsorption of Cr (VI).

Isotherm models	Parameters	Isotherm constants
Langmuir	Q_0 (mg g^{-1})	181.4
	b	0.2571
	R^2	0.960
	R_L	0.0026
Freundlich	K_F (mg g^{-1})	17.56
	n (g L^{-1})	1.268
	R^2	0.179
Dubinin and Radushkevick	Q_0 (mg g^{-1})	15.15
	K_{DR} (mol^2 kJ^{-2})	3.8
	R^2	0.998
	E (kJ mol^{-1})	6.7
Tempkin	b_T	1.55
	B_T (kJ mol^{-1})	1.59
	K_T (L mg^{-1})	4.93
	R^2	0.950

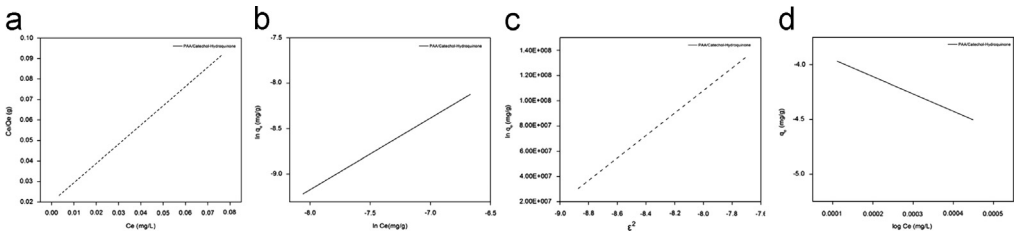

Fig. 5. Linear fit for adsorption isotherms. (a) Langmuir model, (b) Freundlich model (c) Dubin and Radushkevich model and (d) Temkin model.

PAA. The adsorption equilibrium was attained at the 6th hour; initially the metal ions reach the boundary layer and then diffuse through the surface of the modified PAA containing the dihydroxybenzene moieties and then diffuse into the porous polymeric surface of the adsorbent and it requires relatively longer contact time [34]. The leveling effect of the adsorption may be attributed to the saturation of the active sites on the chemically modified PAA and this is evident from Fig. 4(b).

3.3.3. *Influence of the adsorbent dosage*

Fig. 4(c) represents the effect of adsorbent dosage with the initial concentration of Cr(VI) removal by the chemically modified PAA which was carried out at 15 mg L^{-1}, keeping the pH constant and varying the adsorbent dosage from 100 to 500 mg L^{-1} and the temperature was maintained at 25 °C. At the end of 10th hour, with the adsorbent dosage of 500 mg L^{-1} the maximum adsorption was 99%.

3.3.4. *Adsorption isothermal studies*

Table 1 depicts the values of regression coefficients obtained from these models and these were used as the fitting criteria to find out the isotherms. It was found that Chromium (VI) at the initial concentration of 15 mg L^{-1} and PAA/Catechol–Hydroquinone have the linear form (Fig. 5(a)) of the isotherm and high correlation with the Langmuir isotherm models indicating that monolayer adsorption exists and this may be due to heterogeneity of the moieties present in the polymer. The essential characterization of Langmuir isotherm can be explained in terms of the dimensionless constant separation factor R_L. R_L is a positive whose magnitude determines the feasibility of the adsorption process. The R_L values for the different initial concentrations $0 < R_L < 1$ [35] indicate

favorable adsorption of Cr (VI) onto the modified PAA. The linear fit of Freundlich isotherm shown in Fig. 5(b) has least correlation coefficient which concludes that multi-layer adsorption does not exist.

Dubinin and Radushkevick isotherm was applied to estimate the mean free energy path of adsorption (E). From Table 1 and linear fit shown in Fig. 5(c) it can be deduced that the chemically modified PAA follows physical adsorption with endothermic reaction [36]. At lower energy, the percentage of adsorption was found to be higher with the Q_0 value of 15.15 mg g^{-1}.

The Temkin isothermal model is applicable to evaluate the adsorption potential of the applied adsorbents for adsorbate ions. The lower binding energy value calculated through Fig. 5(d) indicates the existence of strong interaction of Cr (VI) ions with the adsorbent surface. The isotherm constants given in Table 1 support the effect of pH on the ion exchange mechanism which is predominant in Cr (VI) adsorption process [37]. The decrease in q_e with increase in adsorbent dosage is due to the unsaturation of the adsorption sites through the adsorption reaction. The particle interaction such as aggregation, resulting from high adsorbent concentration leads to decrease in the total surface area of the adsorbent [38].

3.4. Adsorption of chromium (VI) and lead (II) from industrial effluents

The adsorption of the cations from the solution is pH and time dependent and hence the adsorbent dosage of 500 mg L^{-1} maintained at the pH of 1 with the maximum contact time of 10 h was carried out for the adsorption of chromium (VI) and lead (II) from the tannery effluents. The ICP-OES result shows that the adsorption capacity of the chemically modified polymer varied based on the type of heavy metals present in the tannery effluents (Table 2). The removal of chromium and lead ions was found to be 75% and 99% respectively.

3.5. UV spectra

The λ_{max} value at 264 nm is due to n→π* transition of PAA Fig. 6(a). The λ_{max} at 288 nm is due to π→π* transition of aromatic moieties present in the chemically modified polyacrylic acid with catechol–hydroquinone Fig. 6(b) [39]. Fig. 6(c) shows the formation of metal complex at 540 nm with the Diphenyl Carbazide with least absorbance intensity after 1 hour and π→π* transition of the aromatic ring at 308 nm. At the end of 10th hour the absorbance intensity was found to be high at 534 nm, which concludes that all the Cr (VI) had involved in the reaction with Diphenyl Carbazide resulting in red–violet colored complex (Fig. 6(d)) with the π→π* transition at 319 nm.

Table 2
Comparison of percentage adsorption of Cr (VI) and Pb (II) with the concentration before and after treatment of the tannery effluents (1) and (2) from ICP–OES studies.

	Effluent (1)			Effluent (2)		
Metal ions	Before treatment (mg/L)	After treatment (mg/L)	% Adsorbed	Before treatment (mg/L)	After treatment (mg/L)	% Adsorbed
Cr(VI)	7.58	1.936	75	11.35	5.874	48
Pb (II)	21.99	0.0042	99.9	6.79	0.0042	99.9

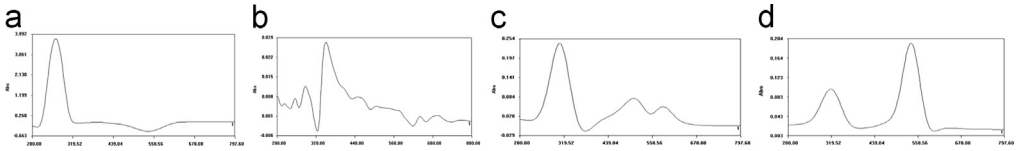

Fig. 6. UV spectra of (a) PAA, (b) chemically modified PAA, (c) chemically modified PAA after treatment at the end of 1 h and (d) chemically modified PAA after treatment at the end of 10 h PAA/Catechol.

3.6. FT-IR spectra

The FT-IR spectra of PAA and chemically modified PAA are shown in Fig. 7(a) and (b), respectively. In the PAA as shown in Fig. 7(a) the peak at 3432 cm^{-1} is due to –OH stretching of the hydroxyl group. The symmetrical and unsymmetrical stretching of the methylene groups are found at 2885 cm^{-1} and 1318 cm^{-1}, respectively. The carbonyl C═O stretching frequency is observed at 1704 cm^{-1}. The strong absorption band at 1599 cm^{-1} is attributed to the C═O stretching vibration of the carboxylate anion present in the polymer. From Fig. 7(b), the intensity of the O–H stretching band centered at 3432 cm^{-1} was enhanced due to the incorporation of dihydroxybenzene. The hydroxyl group of the carboxylic acid present in PAA is replaced by two hydroxyl groups of the dihydroxybenzene. A band that appeared at 1389 cm^{-1} is assigned to O–H deformation vibration mode of the dihydroxybenzene. The band between 1599 and 1704 cm^{-1} that appeared in IR spectrum of PAA is now broadened from 1560 to 1800 cm^{-1} indicating the occurrence of substitution; the aromatic C═C stretching bands expected at 1616 and 1401 cm^{-1} appeared overlapped within this broadened band. Two faint bands can also be noticed at 584 and 1401 cm^{-1} attributable to the angular deformation of C═C and the stretching of C–O, respectively. The presence of bands at 757 $cm^{-1}$and 805 cm^{-1} corresponds to the presence of ortho- and para-substituted aromatic rings namely, catechol and hydroquinone are observed. Infrared spectroscopy can be used to understand the metal ligand bonding states by the changes in vibrational energies of the bonds. In most cases, complexation of the metal induces shifts of the chelating functional groups to higher energies as their non-bonding electrons form a metal–ligand bond. The degree of complexation of the polymer's ligands can generally be estimated by comparing the complexed polymer and uncomplexed polymer spectra [40].

The broad bands around 3300–3500 cm^{-1} in Fig. 7(c) indicate the unchelated hydroxyl group. After treatment the broad bands are shifted from 3418 cm^{-1} to 3495 cm^{-1} which refers to the hydroxyl group chelated with the metal ion; it was observed that the phenolic –OH had been moved from 1389 cm^{-1} to 1379 cm^{-1}. The C–H stretching peak was shifted from 2344 cm^{-1} to 2347 cm^{-1} in chemically modified PAA after the treatment with the heavy metal ions. When compared to the polymer the absorption of the metal ion bands is shifted to a lower value. The bending frequency also showed similar behaviors. These observations suggest that the hydroxyl groups are involved in complexation with the metal ions.

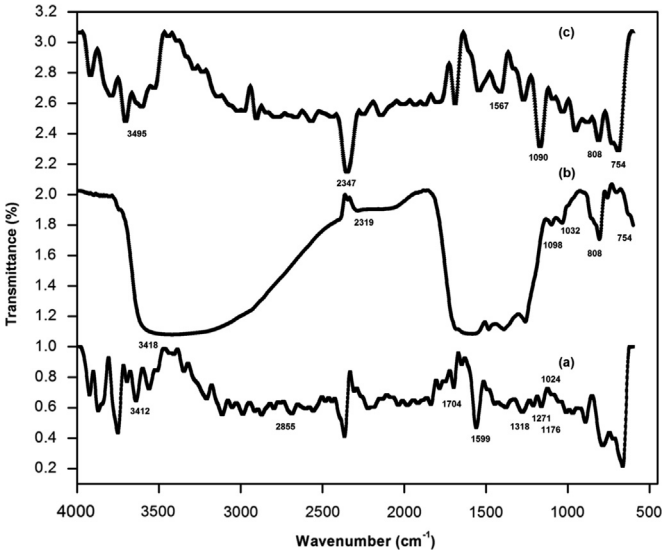

Fig. 7. FT-IR spectra of (a) PAA, (b) chemically modified PAA with Catechol–Hydroquinone before treatment and (c) chemically modified PAA with Catechol–Hydroquinone after treatment.

3.7. Surface morphology

The morphology of the synthesized PAA has lamellar arrangement with amorphous surface nonporous solid microstructure Fig. 8(a). The chemically modified PAA with Catechol–Hydroquinone had been incorporated on to the PAA matrix shown in Fig. 8(b).The polymeric layered arrangement of the adsorbent possesses highly irregular surface and pores, and these pores contribute to a very large surface area. The porous and cavity like arrangement enhances the chemically modified polymers which are suitable for adsorption of heavy metals [41]. Fig. 8(c) shows the SEM images after treatment. The presence of cavities and the porous layered surface of the adsorbent get bulky coated with the adsorbed heavy metal ions. It can be clearly observed that the surface of polymer shape has been changed into a new shiny bulky particle and whitish patches structure after the adsorption of chromium (VI) and lead (II) ions [42].

3.8. Mechanism of heavy metal adsorption

The chelating abilities of PAA/Catechol–Hydroquinone towards Cr(VI) metal ions could be explained based on the structure of the metals' outermost d-orbital electrons. The electron configuration of Cr (VI) is $[Ar]3d^0$. The possible reason for the adsorption of metal ions may include two aspects: firstly, due to the existence of the 3d unoccupied orbital, a lone pair of electrons from the oxygen atom of catechol directly coordinates to the metal center, therefore forming a coordination bond within the compound [43]. Secondly, –OH groups in the catechol structures can form stronger hydrogen bonds with Cr (VI) ions than those hydrogen bonds formed between water and metal ions [44]. Therefore, firm organometallic complexes between chemically modified PAA with catechol moieties present in catechol–hydroquinone and Cr (VI) ions can be formed. In the case of hydroquinone moieties chelation with the adjacent aromatic hydroxyl group is quite possible for the adsorption of Cr (VI). The mechanism has been illustrated in Fig. 9(a).

The electron configuration of Pb^{2+}, $[Xe]4f^{14}5d^{10}6s^2$, contains the $6s^2$ electron pair, which can be either stereochemically active or inactive in Pb(II) compounds. The concepts of stereochemically active and inactive lone pairs arise from the application of VSEPR model to the lighter elements, break down for their heavier congeners as the s-orbitals become less involved in bonding. Consequently, an inert pair of electrons, i.e. the lone pair, will primarily reside in an orbital that is largely spherically symmetrical. The disposition of the ligands may then arise from the directional nature of the p-orbitals involved in bonding, rather than from a localized position for a lone pair, hence Pb–O bond formation will be enhanced [45]. The fully functionalized polymer more effectively binds the Pb^{2+}. The reason for the better overall performance of the fully functionalized system for Pb^{2+} removal can most likely be attributed to the higher number of donors as two oxygen atoms with the aromatic ring were added to each secondary carbon atom of the polymer chain backbone. Selectivity can also be achieved by adding cage-like chelating groups as shown in Fig. 9(b) to the polymer that sterically controls the size of the metal ion that can be ligated. Binding of the metal cation induces precipitation of the polymer–metal complex which can be filtered to remove the metals from solution [46].

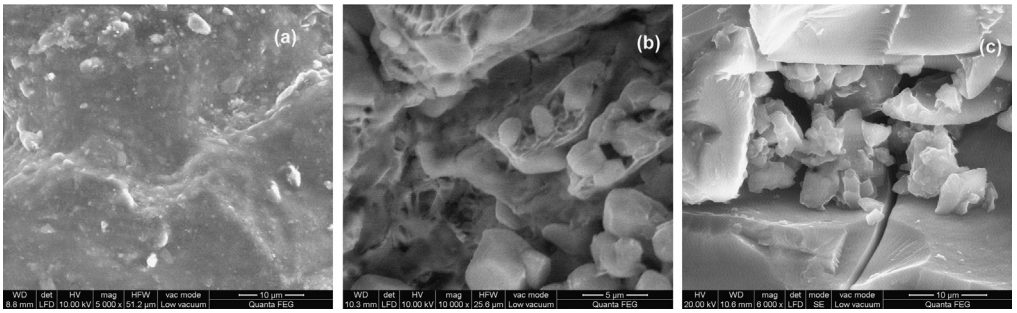

Fig. 8. SEM of (a) PAA, (b) chemically modified PAA before treatment and (c) chemically modified PAA after treatment.

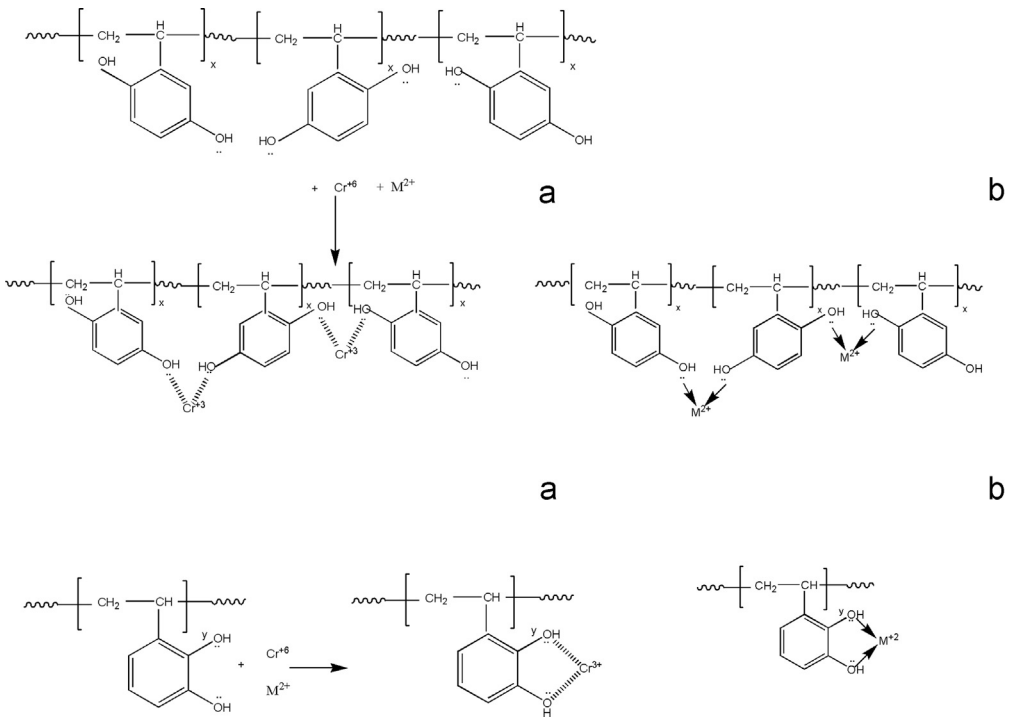

Fig. 9. Mechanism of chemically modified PAA/Catechol–Hydroquinone for heavy metals adsorption. (a) Chromium (VI) ions and (b) Lead (II).

3.9. EDS analysis of the adsorbent after the treatment

The concentration of lead in the effluent (1) was found to be 21.99 mg L^{-1} (Table 1) leading to maximum intensity when compared to chromium concentration which has been evident from the EDS of PAA/Catechol–Hydroquinone after treatment. Fig. 10(a) clearly shows the broad intense doublets are the characteristics of lead assigned to $Pb_{4f7/2}$ that represents the bonding between Pb^{2+} ions with the hydroxyl group of the aromatic moieties [47]. The $Pb_{4f5/2}$ indicates the fixation of lead onto the binding sites of the chemically modified PAA polymeric matrix [48]. The concentration of chromium present in the effluent (2) was 11.35 mg L^{-1}, found to be higher than that of lead. From the EDS spectrum shown in Fig. 10(b) there exists two broad peaks at 0.4 keV and 5.5 KeV of Kα-Cr and Kβ-Cr with 98.48% leading to maximum intensity of chromium when compared to lead.

3.10. Desorption of the heavy metals from the adsorbent

The metal ions loaded on the adsorbent create disposal problem as it is hazardous in nature. Desorption of metal ions from adsorbent and re-generation of the adsorbent is important for the reusability of the adsorbent. For desorption studies metal adsorbed onto the adsorbent was washed with ultra-pure water to remove the unadsorbed loosely attached heavy metal ions to the adsorbent. In order to estimate the recovery of Cr(VI) and Pb (II) from the chemically modified PAA, desorption with 1 M sodium hydroxide was performed [49]. The effect of adsorbent with respective to time is illustrated in Fig. 11. At the end of 5th hour, the adsorbed Cr (VI) metal ions recovered from PAA/Catechol–Hydroquinone were 96% which proves the efficiency of the chemically modified polymers as an adsorbent. On comparison between bioadsorbent [50] and the chemically modified PAA, the chemically modified PAA shows maximum adsorption and the used adsorbent dosage was recovered.

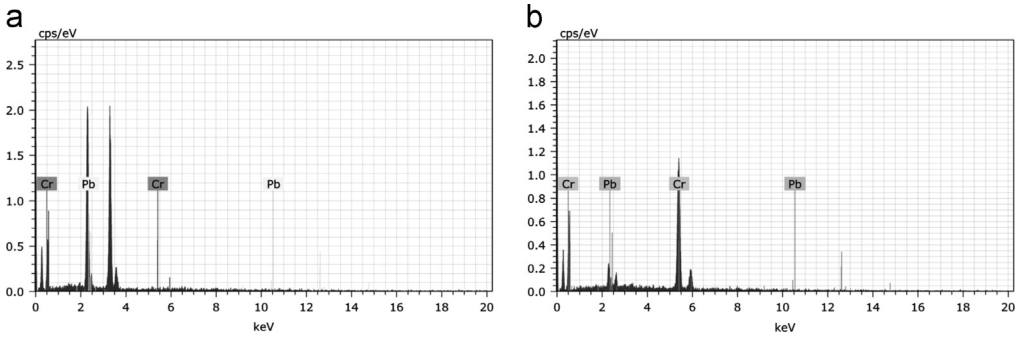

Fig. 10. EDS spectra of the adsorbent chemically modified PAA/Catechol–Hydroquinone after treatment with the tannery (a) Effluent (1) and (b) Effluent (2). (adsorbent dosage 500 mg L^{-1} pH=1, contact time 10 h temperature=25 °C).

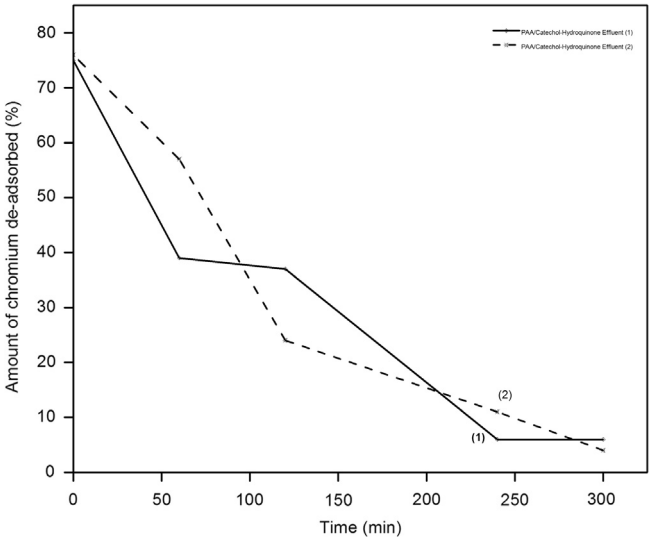

Fig. 11. Desorption profile of Cr (VI) ions adsorbed on chemically modified PAA from the tannery effluent (1) and effluent (2) with contact time.

4. Conclusion

The present work explained the synthesis and characterization of PAA chemically modified with catechol–hydroquinone and their novel approach on the capability and effectiveness in the adsorption of heavy metals from the tannery effluents. Different isotherm models suggest that the adsorption mechanism is suitable for the heavy metal removal which pollutes the environment. The characterization through SEM-EDS, FT-IR, ICP-OES further confirms the heavy metal removal. The adsorption–desorption cycle results open an area for future applications of the chemically modified PAA. Studies on batch adsorption using tannery effluents to remove chromium (VI) and lead (II) indicate that the adsorbent has a good potential to remove the heavy metal ions from the waste water samples.

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